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Dielectric studies of nanocrystalline copper orthophosphate

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Abstract Nanocrystalline copper orthophosphate $\{Cu_3(PO_4)_2\}$ with different grain sizes was prepared by a simple and efficient method by changing the concentration of the reactants. The grain sizes were determined through X-ray diffraction technique. The dielectric properties of the prepared samples were analyzed as a function of frequency and temperature. It is found that the dielectric constant (ε') and dielectric loss ($\tan\delta$) of all the samples decrease sharply as the frequency is increased and attains a constant low value at higher frequencies. The ac conductivity (σ_{ac}) has a low value at smaller frequencies which increases, attains a maximum value and then decreases as the frequency is increased. A similar nature with lower peaks is observed in the very high frequency region also. There is an upward shift in all these values as the temperature is raised. An additional upward shift is observed when the grain size of the samples is reduced.

Keywords Nanocrystalline materials, reactant concentration, dielectric properties

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1. Introduction

The enhanced dielectric properties of nanocrystalline materials exhibiting unusual properties play a vital role in the development of new materials [1–4]. Not only the electronic, magnetic and optical properties but also catalytic and electrical properties of nanostrucrured materials are much different from those of the bulk form and depend sensitively on size, shape, composition and preparation conditions [5]. The large surface to volume ratio and the variations in geometry and electronic structure have dramatic effects on transport and catalytic properties. The large portion of atoms located at surfaces or interfaces greatly influence the transport of ions and electrons through solids. In addition, short-range rearrangement or redistribution of ions and electrons may cause electrical or chemical polarization. This effect is more pronounced or even becomes dominant in nanophase dielectric materials. Each interface will polarize in its unique way when the system is subjected to an applied electric field [6]. Studies on the effect of temperature and frequency on the dielectric behaviour and ac electrical conductivity offer valuable information about conduction phenomenon in nanostructured materials [7]. Dielectric behaviour can effectively be used to study the electrical properties of grain boundaries, since majority of atoms of nanomaterials reside in grain boundaries [8,9]. The origin of resistance or capacitance, its dispersion with small signal frequencies and the role of defects may also obtain from these studies [10]. This paper reports the study of the effect of temperature and frequency on the dielectric constant, dielectric loss and ac electrical conductivity of nanocrystalline copper orthophosphate $\{Cu_3(PO_4)_2\}$ prepared in different grain sizes.

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2. Experimental

Nanocrystalline copper orthophosphate of different grain sizes were prepared by adding stoichiometric amounts of copper nitrate, 10%(w/v) aqueous solution of PVA (the matrix) and the aqueous solution of sucrose (the fuel) and then evaporated to a viscous liquid, as described in the literature [11]. This fluffy, voluminous, carbonaceous, pyrolysed mass is then thermolysed to get the nanosized powders. The carbonaceous precursor powders are then grounded and annealed at 600 °C for 5 hours. The crystal structure and particle size were determined by X-ray powder diffraction technique [12]. The nanosized samples were consolidated into pellets of diameter 13 mm and thickness 1-2 mm at a pressure of ~0.4 GPa. Capacitance (C_p), dielectric constant (ε'), dielectric loss tangent ($\tan\delta$) and ac conductivity

(σ_{ac}) were obtained using a computer controlled Hewlett – Packard 4192 A impedance analyzer [13]. The measurements were carried out at different frequencies from 100 Hz to 3 MHz over the temperature range from 300 K to 373 K.

3. Results and discussion

The X-ray diffraction pattern of nanocrystalline copper orthophosphate powder of reactant concentrations 1.0 mL^{-1}, 0.5 mL^{-1} and 0.1 mL^{-1} (hereafter referred to as samples S1, S2 and S3) are shown in Figure 1. The temperatures of heat treatment significantly influence the reactivity and particle size. The sharp and single X-ray diffraction peaks in the XRD pattern of $Cu_3(PO_4)_2$ powder samples suggest the formation of single phase compounds. The particle sizes were estimated from the line broadening of the diffraction peaks using Scherrer formula and were found to be 28 nm, 26 nm and 23 nm for samples S1, S2 and S3 respectively. Even though the size of the particles is not much different from each other and may be assumed within the range of experimental error, there is appreciable change in the dielectric properties of the present sample when the grain size is changed. This observation clearly indicates that even small changes in particle size may lead to measurable changes in the physical properties of nanostructered materials.

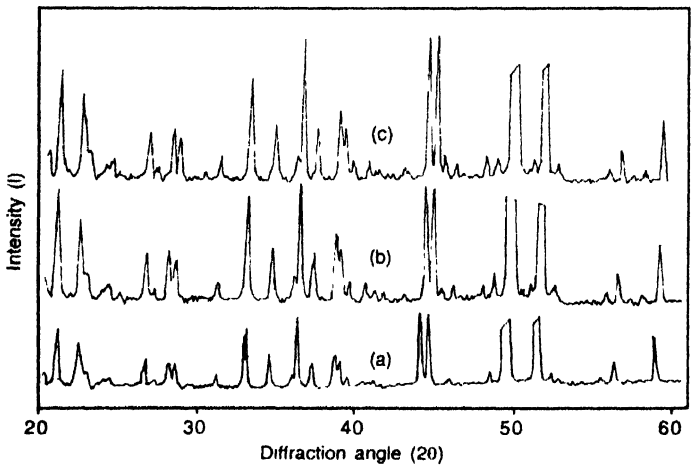

Figure 1. The X- ray diffraction spectra of nanocrystalline copper orthophosphate samples (a) sample S1, (b) sample S2 and (c) sample S3, annealed at 600 °C for 5 Hrs.

The variation of dielectric constant (ε') with frequency of the applied field for temperatures from 300 K to 373 K of sample S1 is shown in Figure 2 (a). It is found that the dielectric constant, for all temperatures, has high value at low frequencies, which decreases as the frequency increases and attains a constant value at higher frequencies. For 300 K, the value of ε' is 607 at 100 Hz which decreased to 28 at 100 KHz. The corresponding values for 373 K are 1312 at 100 Hz and 28 at 100 KHz respectively. The nature is similar for the other samples also, but the values are shifted upwards when the grain size is decreased. Figure 2 (b) shows the corresponding variations at 300 K. The value of ε' changed from 607 at 100 Hz to 43 at 10 KHz for sample S1 while it is from 846 to 52 for sample S2 and from 1120 to 59 for sample S3 respectively. The value of ε' at still higher frequencies remains almost the same at about 28 for all samples.

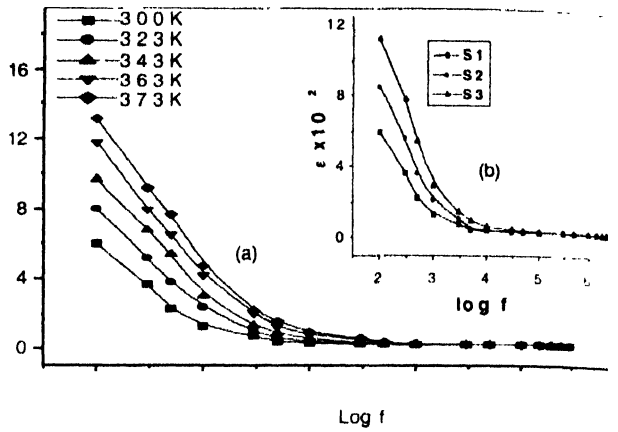

Figure 2. Variation of dielectric constant (ε') with frequency (a) sample S1 at different temperatures and (b) samples S1, S2 and S3 at 300 K.

The variation of dielectric loss (tan δ) of sample S1 as a function of frequency and temperature is shown in Figure 3 (a). The nature of variation of tan δ is almost similar to that of ε'. For 300 K, tan δ has a value of 5.7 at 100 Hz, which decreases to 0.5 at 100 KHz and remains almost at the same constant low value at higher frequencies. At 373 K, the corresponding variation is from 13.26 to 1.33. The variation of tan δ with frequency at 300 K for different grain sizes is shown in Figure 3 (b). At 100 Hz, the value is 5.23 for S1, which increases to 7.72 for S2 and 8.93 for S3 respectively.

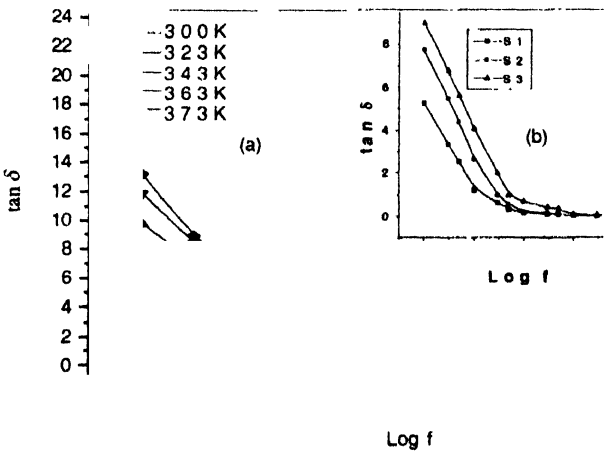

Figure 3. Variation of loss tangent (tan δ) with frequency of (a) sample S1 at different temperatures and (b) samples S1, S2 and S3 at 300 K

According to theory, the dielectric behaviour of nanostructured materials is primarily due to different types of polarizations present in the material [13]. Nanocrystalline materials posses enormous number of interfaces, and the large number of defects present in these interfaces can cause a change of positive or negative space charge distribution. When an electric field is applied these space charges move and are trapped

by these defects resulting in the formation of dipole moments. This is called space charge polarization. Interfaces in nanostructured materials posses many oxygen or nitrogen ion vacancies, which are equivalent to positive charges giving dipole moments. Exposed to an electric field, these dipoles will rotate, giving a resultant dipole moment in the direction of the applied field. This is called rotation direction polarization [14]. Thus, the high value of ε' in the present study at low frequencies, is mainly due to space charge polarization and rotation direction polarization [13-15].

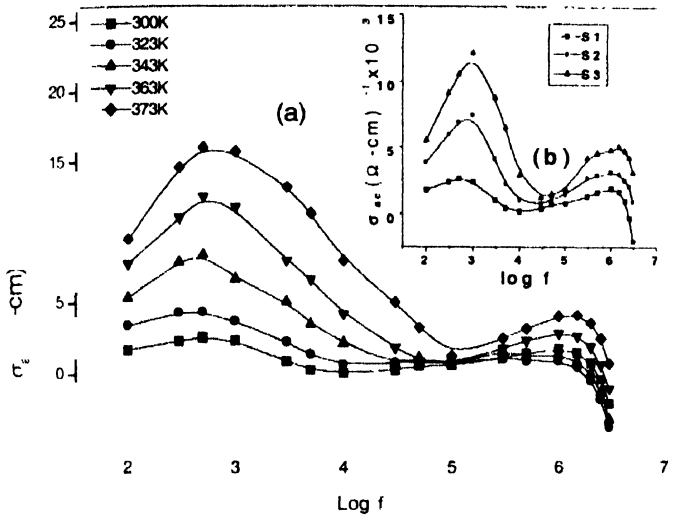

Figure 4. Variation of ac conductivity (σ_{ac}) with frequency of (a) sample S1 at different temperatures and (b) samples S1, S2 and S3 at 300 K

The dielectric constant (ε') initially decreases rapidly with increase in frequency but remains fairly constant at higher frequencies for all the samples. This is due to the fact that beyond a certain frequency of the applied field, the electron exchange does not follow the alternating field [16], and hence the polarization decreases resulting a decrease in ε'. As temperature increases, more and more dipoles will be oriented [17], resulting an increase in the value of the dipole moment. This is why ε' increases with increase in temperature for fixed frequencies.

There is a strong correlation between the conduction mechanism and the dielectric behaviour. The conduction mechanism is due to hopping of electrons; as such when the hopping frequency is nearly equal to the frequency of the externally applied electric field, a maximum of loss tangent may be observed [18]. In nanophase materials, the inhomogenities present in the interface layers produce an absorption current [19] resulting in a dielectric loss. This absorption current decreases with increase in frequency of the applied field, resulting the dielectric loss to be reduced of as shown in Figure 3(a). The hopping or jumping probability per unit time increases with increase in temperature [18]. Correspondingly, the loss tangent also increases. The variation of tan δ for different grain sizes (shown in Figure 3(b)) is due to size effect [13]. From X-ray line broadening studies, it is found that the particle size diminishes as the reactant concentration is reduced (Figure 1). Even though the change in particle size is very small, it leads to measurable changes in the values of ε' and tan δ. The volume percentage of interface boundaries and therefore the amount of defects that cause the various types of polarizations, increase as the particle size is reduced This explains the upward shift in the values of dielectric constant and dielectric loss tangent with respect to reduction in particle size

The variation of ac electrical conductivity (σ_{ac}) as a function of frequency and temperature for sample S1 is shown in Figure 4 (a). At low frequencies, σ_{ac} has a small value, which increases as the frequency increases, reaches a maximum and then decreases with further increase in frequency up to about 1 MHz. A similar variation of ac electrical conductivity with reduced values is observed in the high frequency region (> 1 MHz) as shown in the same figure. The nature is similar for other temperatures, but the values are shifted upwards as the temperature is raised. The maximum value of σ_{ac} at 300 K is 2.6 $\times$ 10^{-3} while the corresponding value of σ_{ac} at 373 K is 16 $\times$ 10^{-3}. The nature of variation of σ_{ac} for samples S2 and S3 at 300 K is shown in Figure 4(b). For sample S1, the maximum value is 2.6 x10^{-3} while the corresponding values for samples S2 and S3, are 7.45 $\times$ 10^{-3} and 12.1 $\times$ 10^{-3} respectively.

The ac conductivity σ_{ac} is obtained from the data of dielectric constant (ε') and loss tangent (tan δ) using the relation

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta, \qquad (1)$$

where ε_0 is the permittivity of vacuum and $\omega (= 2\pi f)$ the angular frequency [17]. Thus, σ_{ac} depends strongly on the frequency of the applied field. The conductivity initially increases with frequency, reaches a maximum and then decreases with frequency for all temperatures.

Electrical conductivity in copper orthophosphate is believed to arise through hopping of electrons between ions in different vacancy states [20]. The sample can carry a current due to an electron moving from a Cu^+ to a Cu^{2+} site. The dispersion in conductivity confirms the existence of electron hopping around lattice imperfections.

σ_{ac} is much more sensitive to temperature in the higher temperature regime than the lower temperature regime. The low temperature ac conduction can be explained using bipolar hopping mechanism whereas the high temperature behaviour is due to thermally activated single polaron hopping [21]. In copper orthophosphate, conductivity increases with the ratio $C = Cu^+/Cu_{total}$ [22, 23]. The effect is a consequence of ionic conduction of Cu+ ions. In other words, $Cu_3(PO_4)_2$ exhibits a 'mixed conduction' phenomenon in which ionic conduction as well as electronic conduction occur.

The classical transport theory cannot be applied in the case of nanostructured materials, and striking new phenomena such as universal conductivity fluctuations were discovered. According to Elliot's barrier hopping model, the ac conductivity is given as

$$\sigma_{ac} = n\pi^2 NN_p \varepsilon' \omega R_\omega^6 / 24, \qquad (2)$$

where n is the number of polarons involved in the hopping process, NN_p is proportional to the square of the concentration of states, ε' is the dielectric constant and R_ω is the hopping distance [21]. When the grain size of the sample is reduced, the hopping distance increases which increases σ_{ac} as is evident from the equation. The five-fold increase of σ_{ac} when the grain size of the sample is reduced from 28 nm to 23 nm in the present study, is a direct confirmation of this theory.

4. Conclusion

Nanocrystalline $Cu_3(PO_4)_2$ samples of different grain sizes were prepared and the particle sizes were determined from X-ray diffraction spectra. The dielectric properties of these samples were analyzed as a function of frequencies from 100 Hz to 3 MHz and temperature ranging from 300 K to 373 K. As the frequency is increased, ε' and tan δ decrease sharply and attain small constant values. The nature remains the same when the temperature is raised but the values are shifted upwards. σ_{ac} strongly depends on frequency and temperature. The peculiar nature of σ_{ac} is thoroughly investigated as a function of frequency and temperature. There is an additional upward shift in the values of ε', tan δ and σ_{ac} when the grain size of the sample is reduced.

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